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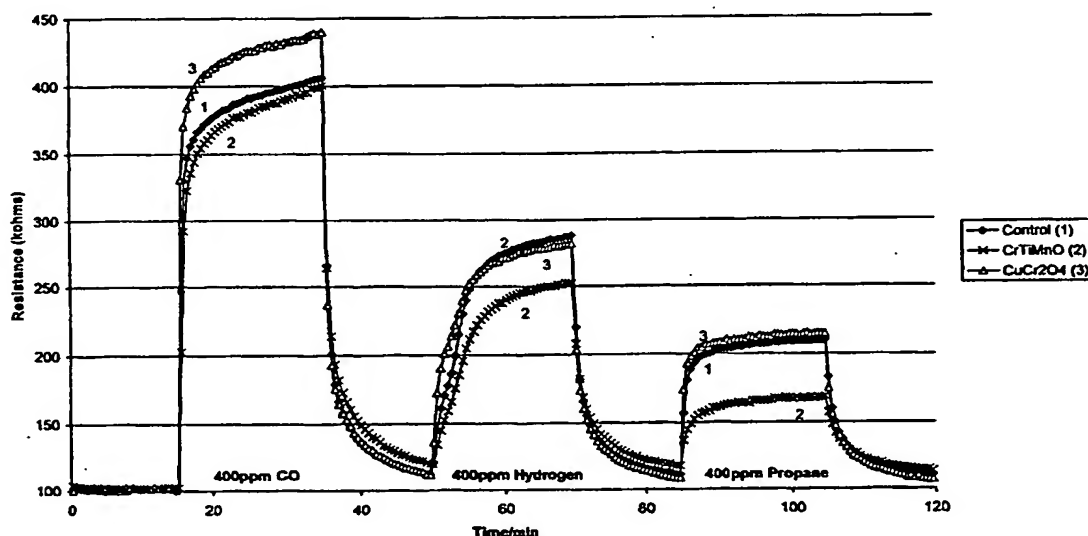
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(54) Title: GAS SENSORS



(57) Abstract: Semiconductor gas sensors with improved selectivity to target gases are provided by having a semiconductor gas-sensing layer and a layer thereon of microporous ceramic oxide having catalytic activity.

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Gas Sensors

Amongst the many technical challenges facing manufacturers of semiconductor sensors/detectors is the need to avoid false alarms. The common cause of false alarms is the presence in the vicinity of the detector of a gas (so-called interference gas) to which the detector responds in a way similar to that for the target gas. To improve the specificity of the detector, one common approach for gas detectors based on semiconductor sensors is to employ a filter material such as activated carbon. Protection against the more common interference gases is achieved provided their concentration is not too high so as to overwhelm the filter. However, this approach suffers from a number of disadvantages, such as a finite absorption capacity, an increased response time and a specificity which may not suit all sensors: carbon blocks hydrocarbons, alcohols and hexamethyldisiloxane (HMDS) but is less adsorbent to ammonia, carbon monoxide, hydrogen and methane.

Other approaches to provide selectivity have been cited in the literature. One such approach is to use sophisticated two-temperature operation modes, as described in US5517182. The sensor surface is purged at the at the higher temperature, while differentiation between the various gases is achieved at the lower temperature by virtue of the faster rate of response of the smaller molecules, such as CO. Another approach is to dope the semiconductor with another oxide so as to enhance its catalytic activity towards the target gas while suppressing it towards other gases (1, 2). This approach requires that the surface electrical properties of the semiconductor are not adversely affected. Enrichment of the surface of the semiconductor grains with a catalyst such as platinum or palladium is still another approach (1, 2). Increased sensitisation has been reported but as with all technologies revolving around noble metal catalysts, poisoning of the noble metal is a potential weakness.

A third approach is to use a coating over the sensor to promote combustion of the heavier gases, which in many cases constitute the interferent gases, prior to reaching the "sensing" layer (2,3). DE19708770 describes the use of a catalytic pre-oxidation filter, comprised of a thick porous layer of Ga_2O_3 above a thin-film Ga_2O_3 gas sensor, for detecting methane. The presence of the pre-oxidation filter is claimed to eliminate cross-

sensitivities to ethanol and to other organic interferent gases. EP0280540 describes the use of an outer catalyst layer fabricated of either conductive or non-conductive material to promote combustion of interferent gases. The conductive material is tin oxide impregnated with Pt or Pd and requires a porous glass layer positioned between the sensing material and the filter layer. The non-conductive material is Pt- or Pd-doped alumina and does not require the porous glass layer. In these examples, increased specificity is achieved primarily by reducing or suppressing the response to the interferent gas through accelerated combustion while the response to the target gas remains unaffected. Elsewhere (4, 5), the use of coatings have been shown to provide a significant enhancement in sensitivity to simple mobile gases, such as hydrogen and carbon monoxide. Here the coatings which are applied in a dense manner, act to slow down the diffusion of oxygen to the sensing layer while the inward fluxes of the faster diffusing hydrogen and carbon monoxide are relatively unchanged. The resulting low oxygen partial pressure in the interior regions is responsible for the higher sensitivities observed for hydrogen and carbon monoxide. Accordingly, the teaching in the prior art suggests that coatings are beneficial in providing selectivity where the target gas is a small molecule and the interferent gas is a larger molecule.

We have now found that if we deposit a microporous coating of a ceramic oxide powder having catalytic activity onto the semiconductor layer, amplification of the response to the heavier gas is possible. We have also found in certain cases that the coating suppresses all gas responses but more so, the responses to the lighter gases. The microporous layer is in intimate contact with the underlying semiconductor layer and, therefore, becomes "hot" on powering up the sensor. As such, its catalytic activity is increased. The ceramic powder does not contain any precious metal such as Pt or Pd and thereby, is resistant to a loss in activity through poisoning.

The ceramic material is oxide in nature and is of the form AO, ABO or ABCO where the cations A, B, C are from the First Transition Series of elements and/or may also come from one of the following: La, Ce, Pr, Zr, Mo, W, Al, Si, Sn, Pb and Bi. The approach avoids altering the electrical characteristics of the semiconductor, as the sensing layer /electrode geometry is chosen so that the coating material is outside the area interrogated by the field lines from the electrodes (6). The approach may be used as

the sole filtering method or in association with a carbon filter. Increased specificity is achieved through amplification of the response to the target gas without changing the response to the interferent gas (or in some cases suppressing it), or, through a reduced suppression of the response to the target gas compared to those of the interferent gases.

The choice of the ceramic powder used in the coating will depend on the particular target gas. Thus, one can increase the sensitivity to a target gas through careful selection of the coating material. For example if the target gas is propane - a requirement in fuel cells or where vehicles/appliances are powered by liquid petroleum gas (LPG) - the use of NiO, Cr₂O₃ or (Fe, Cr)₂O₃ coatings would be recommended to amplify the sensor response over the likely contaminants, hydrogen and CO. Alternatively, if the application is to detect CO in a domestic environment, the use of CuCr₂O₄ or CrTiMinO coatings is preferable.

The microporous layer may be of the same material as the sensing layer itself. However, as this amounts effectively to increasing the thickness of the sensing layer, significant changes in the relative sensitivities do not occur. Adhesion between the coating and the underlying sensing oxide can be problematic if there are large differences in thermal expansion, with spallation of the coating occurring. Methods familiar to those skilled in the art such as additions of thermal expansion modifiers, using lower coating thicknesses and firing to lower temperatures can be used to minimise the build up of thermal stresses and, thus, improve adhesion.

Examples

In the Examples that follow, the materials investigated are described in Table 1, while the results highlighting the degree of selectivity are described in Table 2 and Table 3.

A semiconductor sensor based on the Cr-Ti-O system as the sensing oxide, as described in WO 95/00836, was used in all the examples. The Cr-Ti-O system is a p-type material and undergoes an increase in electrical resistance in the presence of reducing gases. The sensor build is described in various Capteur Sensors' product data sheets for the G series of sensors for detecting carbon monoxide, for example GS07 and GL07 data sheets. During assembly of the sensors, the semiconductor 90 micron Cr-Ti-O layers were coated with the materials shown in Table 1 by screen printing inks comprised of the

coating materials and a terpinol vehicle system supplied by ESL. The solids loading in the coating inks varied from 66wt% to 50 wt%, depending on the surface area and particle size of the oxide used. Unfired print thickness for each of the coatings are also given in Table 1. The resulting composite structure was co-fired to 800°C prior to assembling into the standard build. As described in the product data sheet, the sensors were powered up alongside standard sensors to approx. 400°C such that the electrical resistances were 100 kohms in 50% RH clean air. Following stabilisation for a period of 20 minutes, the sensors were then exposed to various test gases for 20 minutes with cleaning air steps in between. The test gases used were air - 400ppm CO, air - 200ppm propane, air - 400ppm propane, and air - 400ppm hydrogen. The benefit of improved specificity to propane through amplification of the propane response is shown in Table 2. Comparison should be made with the control (i.e. no coating) and with the CTO-coated sensor.

Table 1: Oxide Materials used as Coatings

| Coating Material | Supplier | Powder Details | Dry Print Thickness (microns) |
|---|-----------------------------------|--|-------------------------------|
| Cr_2O_3 | Johnson Matthey | $D_{50} = 0.2\text{micron}, 7\text{m}^2/\text{g}$ | 100 microns |
| $\text{Fe}_{1.2}\text{Cr}_{0.8}\text{O}_3$ | Johnson Matthey | $D_{50} = 0.6\text{micron}, 12\text{m}^2/\text{g}$ | 100 microns |
| Mn_2O_3 | Sigma-Aldrich Company Ltd | -325 mesh | 100 microns |
| SnO_2 - 0.7wt% Sb_2O_3 | Sigma-Aldrich Company Ltd | -325 mesh, $8\text{m}^2/\text{g}$ | 50 microns |
| NiO^* | Sigma-Aldrich Company Ltd | < 10 microns | 60 microns |
| SiO_2^* | Sigma-Aldrich Company Ltd | -325 mesh | 70 microns |
| CuCr_2O_4 -6% BaO | Strem Chemicals Ltd | 45-50 m^2/g | 100 microns |
| $\text{CuCr}_2\text{O}_4^{**}$ | Johnson Matthey | $D_{50} = 1.1\text{micron}, 6\text{m}^2/\text{g}$ | 100 microns |
| $\text{Co}(\text{Cr},\text{Al})_2\text{O}_4$ | Johnson Matthey | $D_{50} = 1.2\text{ microns}, 11\text{m}^2/\text{g}$ | 100 microns |
| CoTi_2O_4 | Johnson Matthey | $D_{50} = 1.7\text{microns}, 7\text{m}^2/\text{g}$ | 100 microns |
| WO_3 | Capteur Sensors and Analysers Ltd | $D_{50} = 0.8\text{ microns}, 2\text{m}^2/\text{g}$ | 60 microns |
| Zeolite 4A ^{***} | The Smart Chemical | $D_{50} = 5\text{ microns}$ | 15 microns |

| | Company | | |
|------------|-----------------------------------|--|-------------|
| Cr-Ti-Mn-O | Capteur Sensors and Analysers Ltd | $D_{50} = 0.8$ microns | 100 microns |
| Cr-Ti-O | Capteur Sensors and Analysers Ltd | $D_{50} = 0.8$ microns, $5\text{m}^2/\text{g}$ | 100 microns |

* Oxide mixed with Cr_2O_3 in the ratio of 4 parts : 1 part of Cr_2O_3 and mixture homogenised by sieving through a 38 micron mesh

** Oxide mixed with Cr_2O_3 in the ratio of 1 parts : 1 part of Cr_2O_3 and mixture homogenised by sieving through a 38 micron mesh

*** Oxide mixed with low-melting lead glass in the ratio of 2 parts to 1 part of lead glass and homogenised by sieving through a 38 micron mesh.

Table 2: Results Showing Amplification Effects of Coatings on Responses to Propane

| Coating | $R_{400\text{ppmP}}/R_{400\text{ppmCO}}^{\wedge}$ | $R_{400\text{ppmP}}/R_{400\text{ppmH}}^{\wedge\wedge}$ |
|---|---|--|
| Cr_2O_3 | .75 - 0.95 | 1.05 |
| $\text{Fe}_{1.2}\text{Cr}_{0.8}\text{O}_3$ | .75 - 0.90 | |
| Mn_2O_3 | .65 | .84 |
| SnO_2 - 0.7wt% Sb_2O_3 | .64 | .86 |
| NiO [*] | 1.13 | 1.18 |
| SiO_2^* | .76 | .85 |
| $\text{Co}(\text{Cr},\text{Al})_2\text{O}_4$ ** | .71 | 1.01 |
| CoTi_2O_4 ** | .58 | .88 |
| WO_3 | .89 | .99 |
| Al_2O_3 | .59 | .80 |
| Zeolite 4A *** | .85 | 1.06 |
| Cr-Ti-O | .61 | .85 |
| Control - no coating | .54 | .73 |

[^] The ratio of the sensor response in 400ppm propane to that in 400ppm CO

^{^^} The ratio of the sensor response in 400ppm propane to that in 400ppm hydrogen

Table 3: Results Showing Effects of Coatings on Selectivity to Carbon Monoxide

| Coating | $R_{400\text{ppmCO}}/R_{400\text{ppmP}}^{\text{S}}$ | $R_{400\text{ppmCO}}/R_{400\text{ppmH}}^{\text{SS}}$ |
|---------------------------|---|--|
| CuCr_2O_4 | 2.38 | 1.69 |

| | | |
|----------------------|------|------|
| Cr-Ti-Mn-O | 2.56 | 1.69 |
| Control - no coating | 1.85 | 1.35 |

^s The ratio of the sensor response in 400ppm CO to that in 400ppm propane

^{ss} The ratio of the sensor response in 400ppm CO to that in 400ppm hydrogen

Example 1 (Figure 1)

On exposure to 200ppm propane at 50% relative humidity, the standard sensors (i.e. no coating) show resistance values of 150 - 170 kohms, while the 100 micron-thick Cr_2O_3 -coated sensors showed enhanced sensitivities with resistance increases to 290 and 330 kohms being observed. This serves to highlight the amplifying effect of Cr_2O_3 on the response to propane.

Example 2 (Figure 2)

As in Example 1, except in this case, Cr_2O_3 coatings of unfired print thicknesses of 50 and 150 microns were also investigated. Following stabilisation in clean air, the sequence of gas steps was 20 minutes in 400 ppm CO, 15 minutes in clean air, 30 minutes in 36 ppm ethanol, followed by 20 minutes in clean air. All gas steps were carried out at 50% RH. As shown in Fig. 2, the coated and uncoated sensors have similar responses to CO but the coating thickness affects the response to ethanol. The standard sensors give a response of 460 - 480 kohms to 36 ppm ethanol. Applying a coating of 50 microns thick reduces the response by 120 - 140 kohms or by 25 - 30 %. For increased thicknesses of 100 and 150 microns, greater reductions in response by 250 - 280 kohms or by 50 - 60% are observed. This example serves to highlight the reduced cross-sensitivity of the Cr_2O_3 -coated Propane/CO sensors to ethanol.

Example 3 (Figure 3)

As in Example 1, but using sensors coated with a range of different ceramic materials, as described in Table 1. The sensors were exposed to the test regime: 10 minutes air, 20 minutes 400ppm Hydrogen, 15 minutes air, 20 minutes 400ppm Propane, 15 minutes air, 20 minutes 400ppm CO followed by 15 minutes in air. The coatings applied have the effect of amplifying the response to propane compared to the interferent gases, hydrogen and CO. The sole exception is the zeolite/glass coating which suppresses the responses to hydrogen and to carbon monoxide more strongly than the response to propane.

Example 4 (Figure 4)

As for Example 3 but using different coating materials (Table 1), showing the effect of amplifying the sensor response to propane.

Example 5 (Figure 5)

In this Example, two coating materials (as described in Table 1) provide selectivity towards carbon monoxide relative to hydrogen and to propane. The test regime used was: 15 minutes air, 400ppm CO, 15 minutes air, 20 minutes 400ppm hydrogen, 15 minutes air, 20 minutes 400ppm propane, 15 minutes air. The CuCr_2O_4 coating provides selectivity through amplification of the response to carbon monoxide unlike the CrTiMnO coating which does not alter the CO response but suppresses the responses to hydrogen and propane.

Example 6 (Figure 6)

A comparison is made between sensors coated with 100 micron-thick Cr_2O_3 and $(\text{Fe, Cr})_2\text{O}_3$ in this Example. The test regime used was 30 minutes air, 40 minutes in 400ppm CO, 40 minutes air, 40 minutes 400ppm propane, 40 minutes air. Both coating materials (Table 1) amplify the propane response by similar amounts relative to the CO response.

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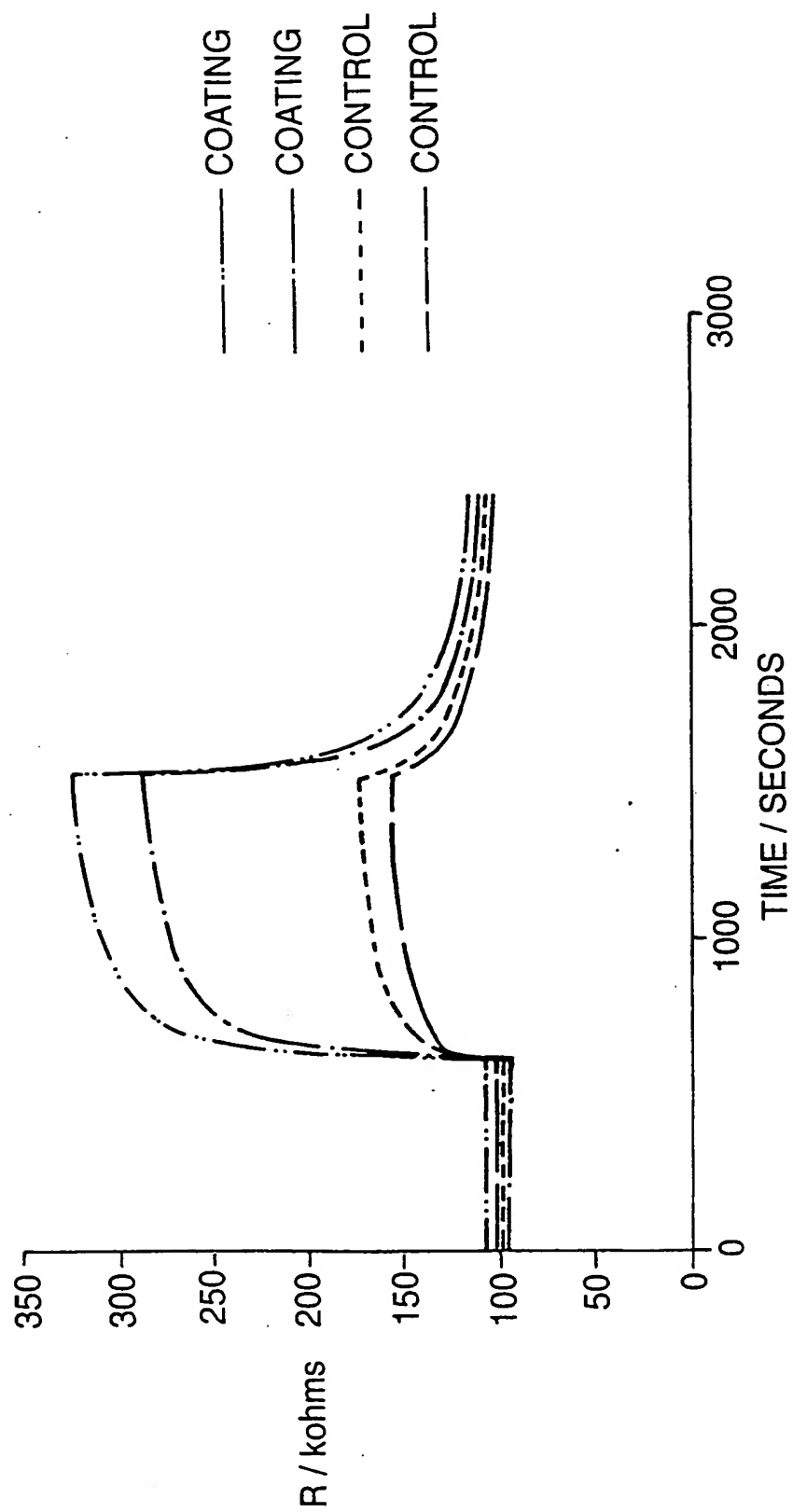
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Claims:-

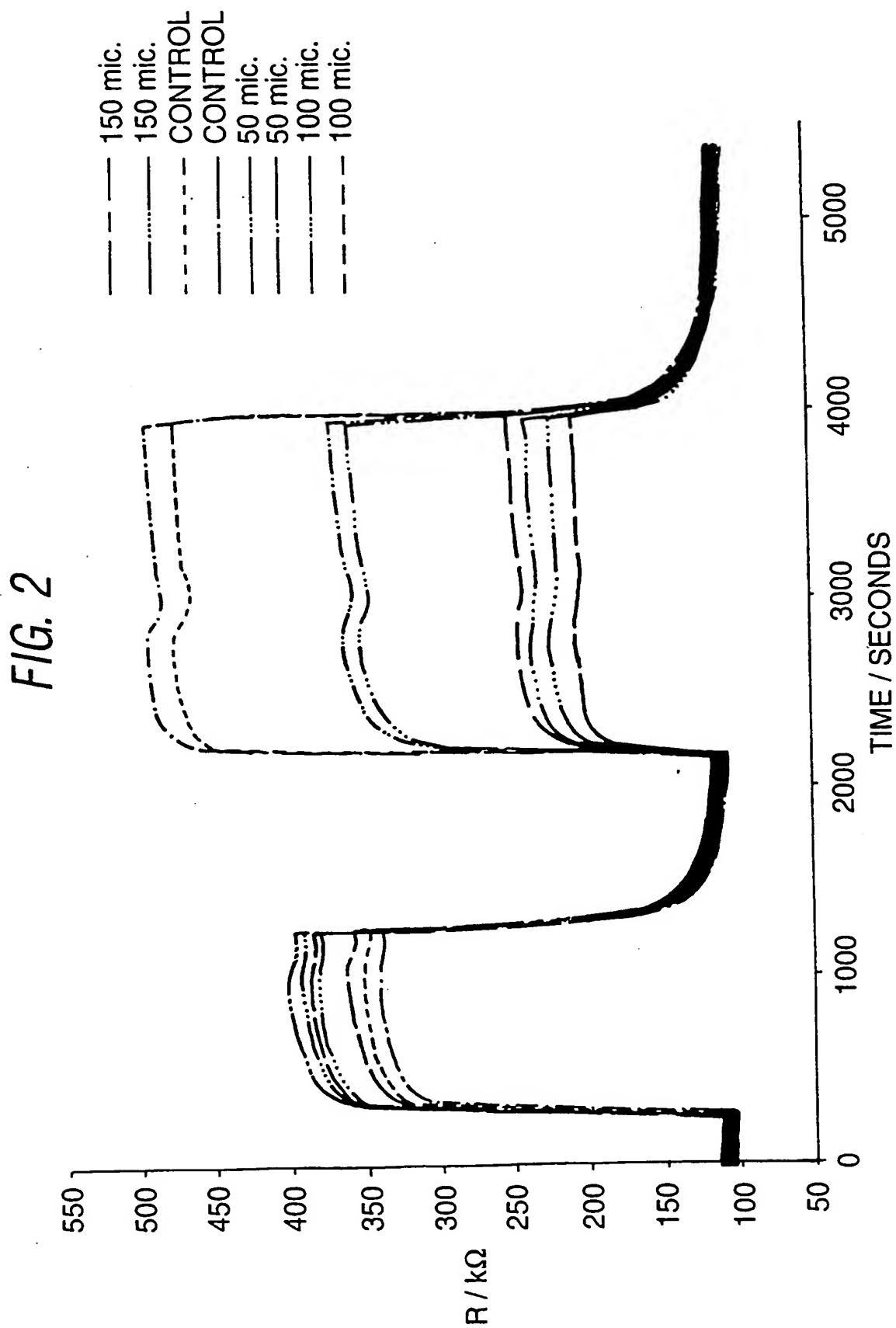
1. A gas sensor having a semiconductor gas-sensing layer and a layer thereon of a microporous ceramic oxide having catalytic activity.
2. A gas sensor according to claim 1 wherein the ceramic oxide is an oxide of one or more first order transition elements and/or one or more of La, Ce, Pr, Zr, Mo, W, Al, Si, Sn, Pb, and Bi.
3. A gas sensor according to claim 2 wherein the ceramic oxide is Cr_2O_3 .
4. A gas sensor according to any of claims 1 to 3 wherein the semiconductor gas-sensing layer is chromium titanate.
5. A gas sensor according to any of claims 1 to 4 in combination with a carbon filter.
6. A method of manufacturing a gas sensor as claimed in any of claims 1 to 5 which comprises screen printing the ceramic oxide onto the semiconductor layer and firing the layer.
7. A method according to claim 6 which comprises initially screenprinting the semiconductor layer onto a substrate and cofiring the semiconductor and ceramic oxide layers.
8. A method according to claim 6 or 7 wherein the ceramic oxide is screen printed with an ink comprising a ceramic oxide powder dispersed in a liquid vehicle.
9. A method according to claim 8 wherein the powder has a surface area of 5 to $50 \text{ m}^2/\text{g}$ and a particle size of 0.001 to 50 microns.

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FIG. 1

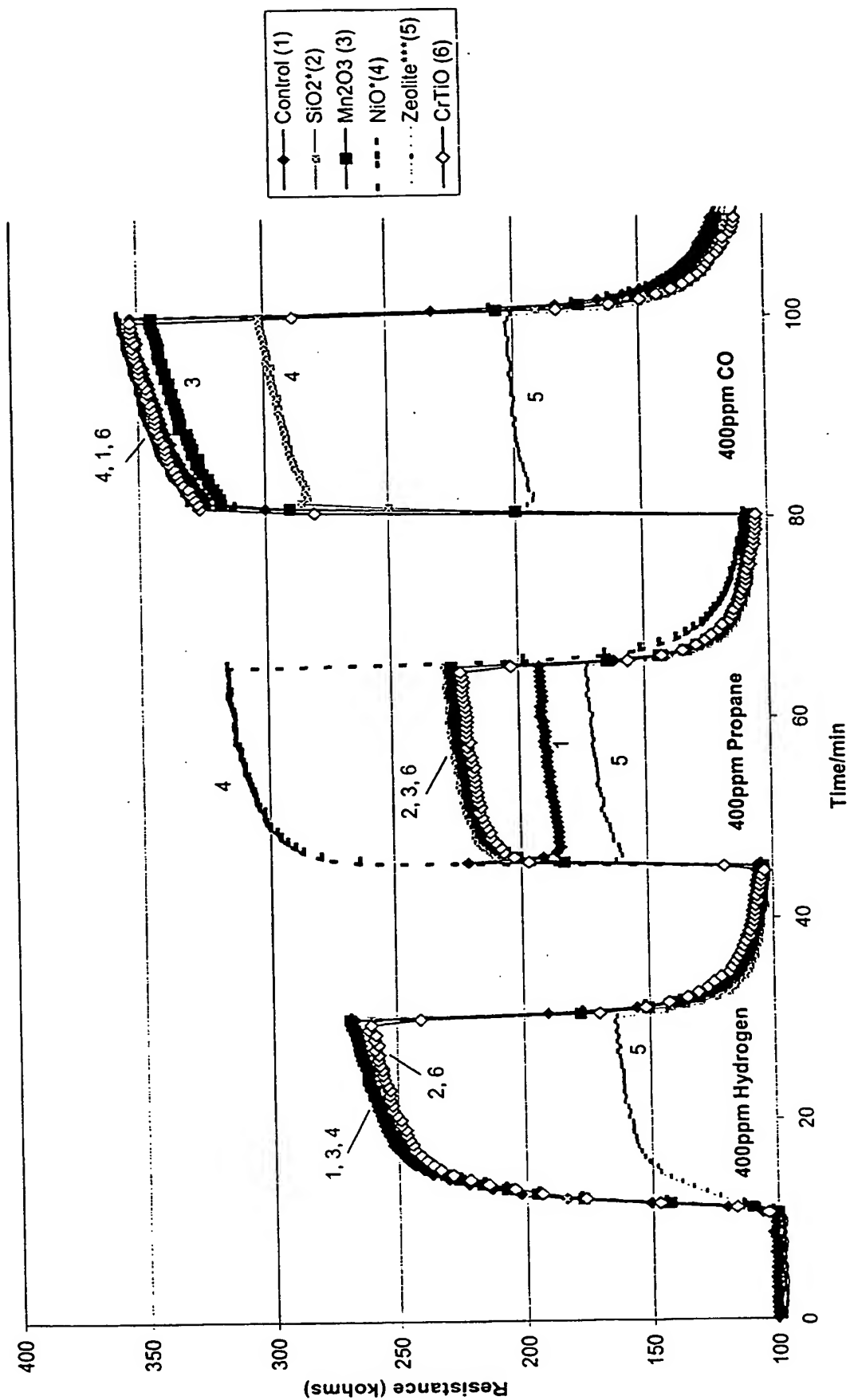


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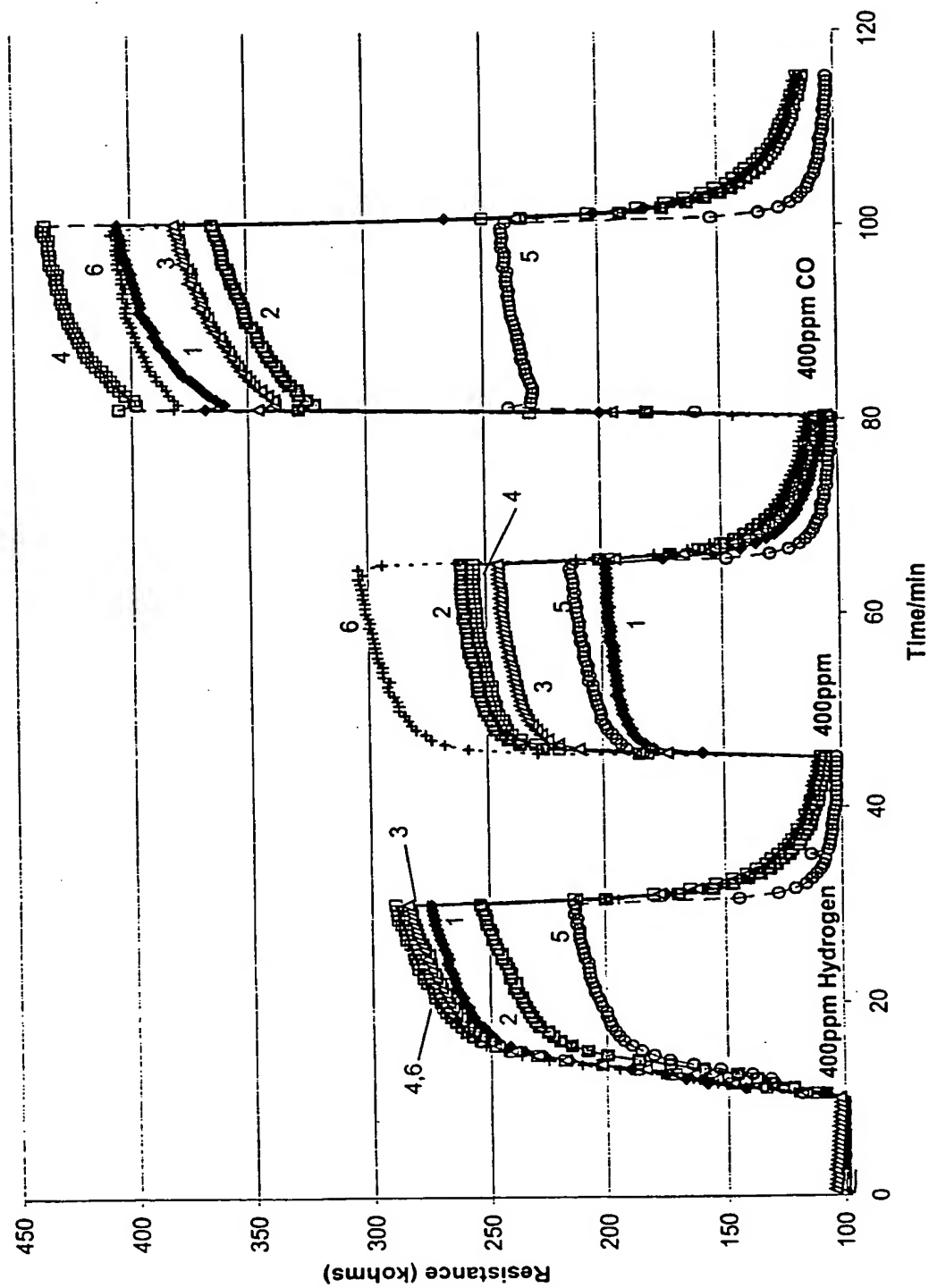
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FIG. 3



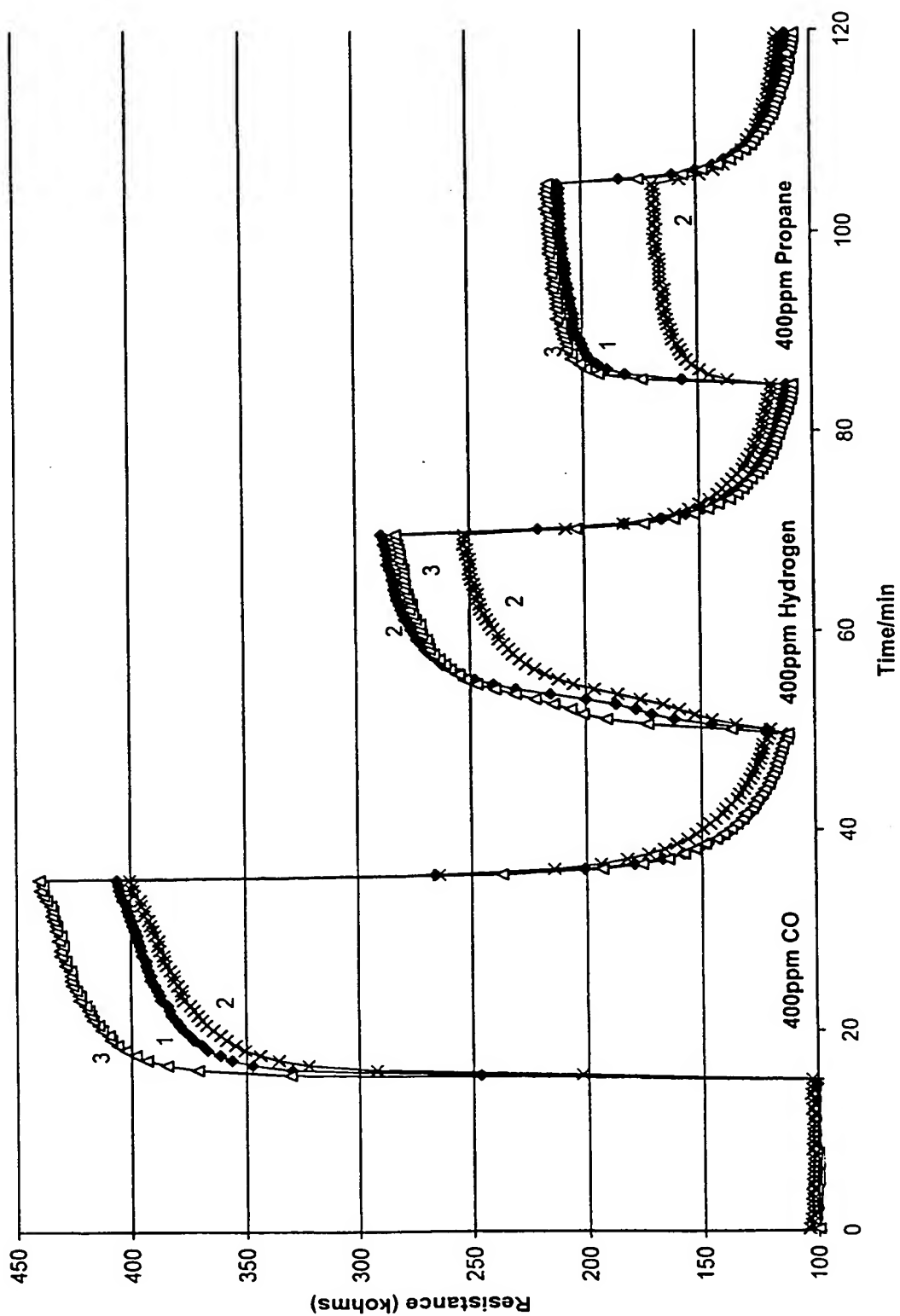
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FIG. 4



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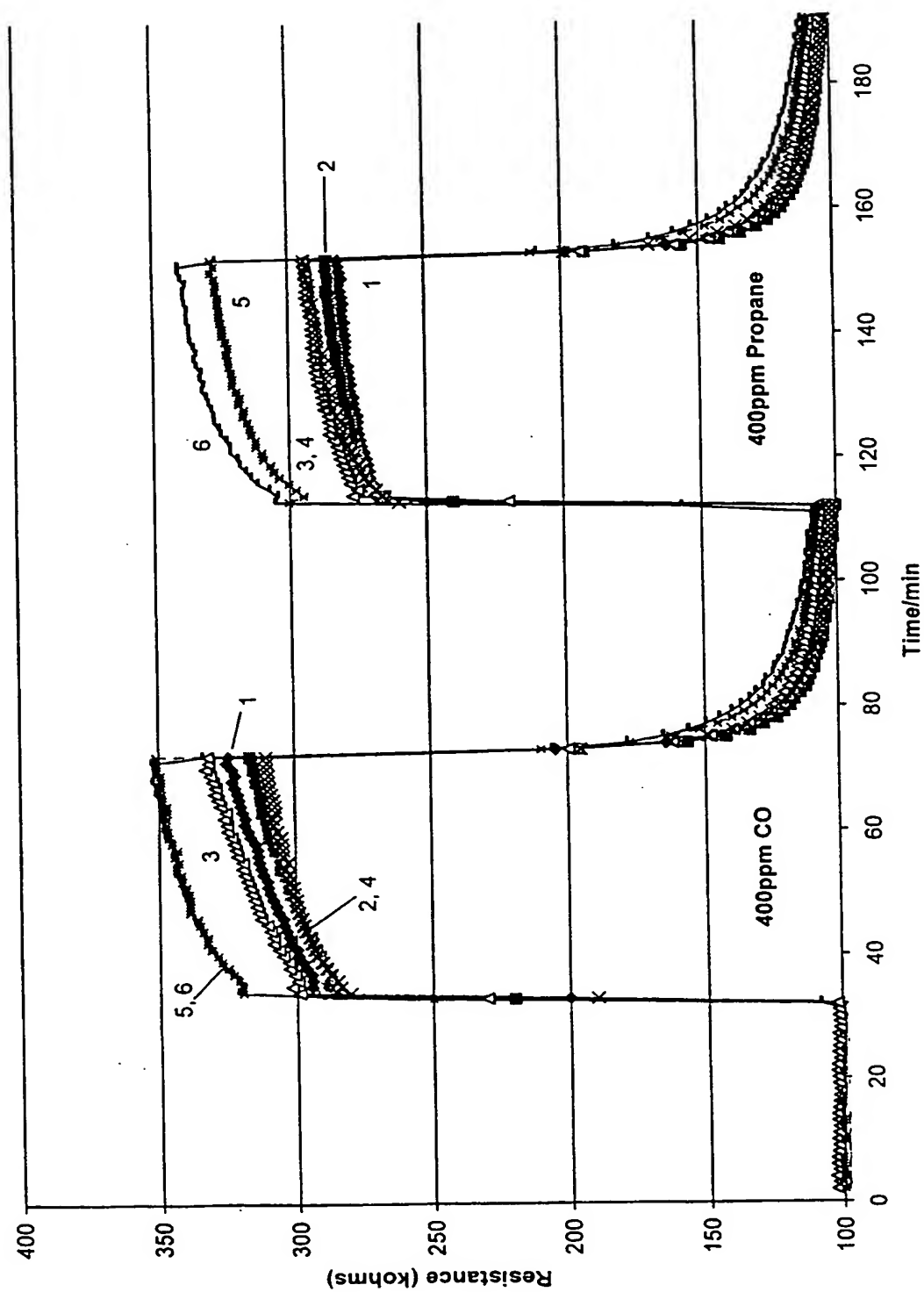
FIG. 5



Control (1)
CrTiMnO (2)
CuCr2O4 (3)

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FIG. 6



INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G01N33/00 G01N27/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

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☒ Further documents are listed in the continuation of box C.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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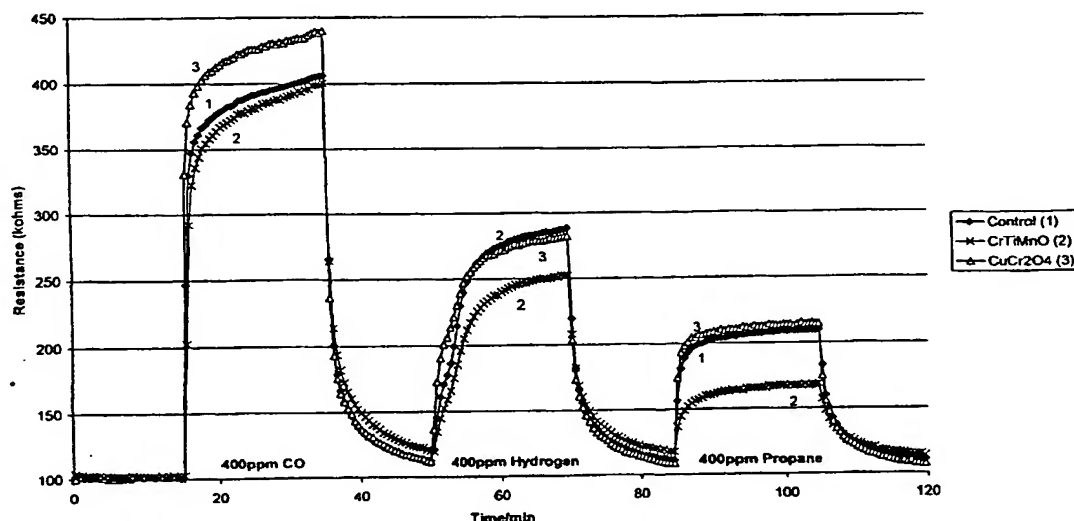
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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: GAS SENSORS



(57) Abstract: Semiconductor gas sensors with improved selectivity to target gases are provided by having a semiconductor gas-sensing layer and a layer thereon of microporous ceramic oxide having catalytic activity.

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